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Goat Cheese Quality in North Macedonia

Erhan Sulejmani

Abstract

The most significant agricultural industry in North Macedonia is the dairy industry, and white-brined cheese is a popular dairy product with a great history and the most selling cheese in the country. Considering the climatic conditions and the experiences of other countries, the Republic of North Macedonia has capacity for adequate development of goat breeding by creating small-to-medium goat farms and application of intensive or semi-intensive goat farming systems. There are various breeds of goats in the Republic of Macedonia such as the domestic Balkan goat, Saanen, and Alpine and crossbreeds between these breeds. The official restriction of goat breeding in the territory of Macedonia in 1947 had disastrous consequences; however, in 1989, goat breeding was again allowed and has increased. There are three most significant kind of cheeses manufactured in Macedonia, like white-brined, beaten, and kashkaval. White cheese in Macedonia (belo sirenje) is a brine cheese type with salty taste and close texture similar to beyaz peynir (a Turkish white cheese).

Keywords: domestic Balkan goat, white cheese, kashkaval, beaten cheese

1. Introduction

The Republic of North Macedonia is a land-locked country in southeastern Europe in the Balkan Peninsula, with 850 km of frontier with five countries: Serbia, Kosovo, Montenegro, Albania, Bulgaria, and Greece. The country has a surface area of 25,713 km². Half of this area (1.26 Mio. ha) is agricultural land, out of which 560,000 ha are classified as cultivated land and 704,000 ha as permanent pastures. Mountainous forest land covers 37% of the country, and about 2% is covered by lakes. Livestock and goat farming is very important in the Polog area, in the foot of the Sharr Mountain. These areas represent a mountain chain stretching from the southern part of Kosovo and northwestern Macedonia to northeastern Albania. The Sharr Mountain represents the largest mountain massive in Macedonia and extends to these geographic coordinates, between 42°41'43" and 42°16'34" north latitude, as well as between 20°34'51" and 21°16'00". The mountain system is about 80 km long and 10–20 kilometers wide. It includes a number of high points, among which the highest peak of the Titov vrh is 2747 m, Mali Turc (2702 m), Ljuboten (2498 m), and Bistra (2641 m).

Goat breeding in Macedonia is defined by spontaneous and continuous development, and with each day, there is major concern of farmers for goat's growth as a market that provides secure subsistence and business. The breed structure of goats in the country is based on the domestic Balkan goat with a certain representation of the Alpine breed goats, Saanen, and crossbreeds of these races. The basic product

obtained from goats is goat's milk (which is commonly processed into white-brined cheese, yogurt, and kashkaval), kids, and goat meat [1]. The official restriction of goat breeding in the territory of Macedonia in 1947 resulted in disastrous consequences, which lasted for more than 40 years. The goats in the entire territory of the former Socialist Republic of Macedonia were slaughtered and rapidly reduced number from 516,800 in 1947 to 47,000 in 1949 or more than 90%. However, in 1989, goat production was again allowed, and since then, the interest of the farmers in goat production has increased [2].

Pacinovski et al. [3] reported that Goat livestock industry has a century-old tradition in Macedonia due to environmental factors and a type of vegetations suitable for goat breeding; wherefore, these animals have provided subsistence of the population in the past centuries. Historically, the number of goats bred in Macedonia was around 500,000 heads, with the law for prohibited goat breeding (Law for Prohibited Goat Breeding, 1948). This law had highly significant negative role in reducing the number of goats in the Republic of Macedonia. Petrovska et al. [4] emphasized that goat breeding in Macedonia is difficult due to a number of factors such as unfavorable racial composition and fragmentation of herds, unorganized and insecure sale of milk and dairy products, shortage of labor, weak and irregular application of selective measures in the herds, and more. However, compared with past years, it can be concluded that there is spontaneous and continuous development of the husbandry industry with growing interest of farmers for goat breeding. The total number of goats the Republic Macedonia is around 80,000 with a tendency to increase.

There are six genotypes (breeds) of goats present in Macedonia in the system for identification and marking of livestock within the Food and Veterinary Agency: domestic Balkan goat, Alpine, Saanen goat, crossbreeds with Alpine, crossbreeds with Saanen goat, and genotype registered under the name of other population. According the same agency, out of the total quantity in 2011, 48% of the total number of goats are domestic Balkan goats, 5.5% are Alpine goats, 7.9% are crossbreeds with Alpine goat, 7.8% are Saanen goats, 3.4% are crossbreeds with Saanen goat, and the rest are recorded as other breeds of goats [5].

According to Pacinovski et al. [6] and the data of the Food and Veterinary Agency, the department for identification and registering of domestic animals, there are six genotypes of goats in the Republic of Macedonia: domestic Balkan goat, Alpine, Saanen, Alpine crossbreed, crossbreeds with Saanen goat, and population registered under the term of other. The most represented goat breed in the country is domestic Balkan goat, with a number of around 38378 goats, goats registered as other with a number of 21772 goats, the number of crossbreeds with Alpine is 6330, Saanen with 6256 goats, Alpine is represented with 4193 and crossbreeds with Saanen are represented with 2735 goats. Balkan goat is well adopted to the existing climate conditions in the country as well as to the existing nutritional resources especially in the hilly mountainous areas of the Republic of Macedonia, which are not suitable for other domestic animals. It is the shrubbery vegetation which is especially attractive to goats. The excellent adaptability of the breed is due to the excellent health condition of goats manifested during the whole year. Compared to the other breeds (Alpine, Saanen, and crossbreeds between the same with other breeds), Balkan goat is extremely resistant to many diseases (chronic, bacterial, etc.). They are especially resistant to emergent climate changes that affect the goat health.

Traditional cheeses represent a cultural heritage and are the result of accumulated empirical knowledge passed from generation to generation [7]. Accurate and precise milk recording is one of the most significant moments for a successful selection of milking goats. In this context, breeders are constantly making efforts to find

the most suitable and cheapest methods for conducting of tests for milk. According to Pacinovski et al. [8], in Macedonia predominate extensive goat dairy industry and machine milking are not widespread throughout the country. There is much to be done about the improvement of goat farms in respect to goat breeding and comprehensive mechanization of farm routines which both increase efficiency of the farms.

2. Milk and cheese analysis

Milk and cheese samples were analyzed in duplicate for moisture, fat, salt, pH, titratable acidity (as percentage of lactic acid), and total nitrogen [9]. Total nitrogen (TN) content was estimated by the Kjeldahl method using a Kjeldahl device (model DS1; Simsek Labortechnik, Ankara, Turkey) [10]. The water-soluble nitrogen (WSN) and 12% TCA-soluble nitrogen (TCA-SN) as percentage of TN and total free amino acid (FAA) of the cheeses were determined [11].

The water-insoluble fractions of the cheeses were freeze-dried and then analyzed by urea-PAGE using a Protean II XI vertical slab gel unit (Bio-Rad Laboratories Ltd., Watford, UK), and the gels were stained directly with Coomassie Brilliant Blue G-250 dye [12, 13].

After destaining using pure water, gel slabs were digitized using a scanner (HP Scanjet software, Scanjet G4010; Hewlett-Packard, Palo Alto, CA). Scans of the electrophoretograms were used to quantify bands using densitometric software (ImageMaster TotalLab Phoretix 1D Pro software; Keel House, Newcastle upon Tyne, UK).

The caseins and peptides were determined quantitatively by integration of peak volumes and areas using the densitometer. The WSN fractions of the cheeses were also freeze-dried for determination of peptide profiles. The analysis was realized by RP-HPLC using a Shimadzu LC 20 AD Prominence HPLC system (Shimadzu Corp., Kyoto, Japan) [14].

Solid-phase microextraction/GC-MS analysis of volatiles. Analysis of the volatiles was performed by a static solid-phase microextraction method, using a GC-MS system (Shimadzu Corp.). The identifications were based on comparing mass spectra of unknown compounds with those in the mass spectral library of John Wiley and Sons Inc. (2005) and the National Institute of Standards and Technology/Environmental Protection Agency/National Institutes of Health (NIST/EPA/NIH 02; <http://www.nist.gov/srd/nist1a.cfm>) mass spectral library. Identifications were also confirmed by comparing retention times with reference standards when available.

A total of 33 authentic standard compounds (Sigma Chemical Co., St. Louis, MO) were used to confirm the identities of volatile compounds in the cheese samples. The concentrations were calculated by the comparison of the peak areas of the internal standard containing mixture of 2-methyl-3-heptanone and 2-methyl-1-pentanoic acid in methanol (Sigma-Aldrich Co.) and unknown compounds. Each compound was expressed in micrograms per 100 g of cheese.

3. Goat milk quality and cheese varieties

Goat breeding is an important livestock branch, and great attention is paid to its development and industrialization in all Mediterranean countries. The composition of milk is of great importance for determining the technological properties of goat milk and for its further processing in a suitable type of cheese. According to the historiographic data, the golden period of the Macedonian livestock breeding was in the middle of the nineteenth century, when there were about 7–9 million sheep and 2 million goats in Macedonia's borders [8].

With the adoption of the Law on Goat Breeding in 1989, the goat again began to take its place in our livestock breeding. Today's situation of goat is heterogeneous, given the fact that the individual producers preserve 1–2 goats, but there are also those who breeds 20–30 goats, while the organized goat farms have 100 or more heads. It is estimated that in our country, there are under 100,000 goats with a major participation in the domestic Balkan goat and in a smaller proportion the Saanen, Alpine, and their half-bred [6].

Accordingly, the milk used for the production of cheese should be of a normal chemical composition in accordance with the rulebook on requirements for the quality of raw milk, quality standards for consumer milk, dairy products and the use of their names, quality and activity of starter cultures, curdling and other specific substances, and the manner of their use, the manner of additional labeling of milk and dairy products, as well as the permitted deviation of weight in relation to the declared [15]. Goat milk is often mixed with the cow or sheep's milk and as such is offered to the dairies so that its nutritional values are not properly valuated. A certain part is processed by farmers in white goat cheese, but due to its specific taste and smell, it consumes a certain number of the population, although it has higher nutritional and therapeutic values compared with other cheeses. Goat breeding has a good perspective, given the good natural conditions, but also because of the fact that goat milk is given greater importance nowadays, especially because of its dietary and nutritional properties.

The quantities of individual ingredients affect the technological characteristics of the curd, as well as the organoleptics and the quality of the finished product [16]. The physical-chemical characteristics of the used milk for the production of the white-brined goat cheese was 3.44 ± 0.10 g/100 g for protein, 3.00 ± 0.24 g/100 g for fat, 11.99 ± 0.17 g/100 g for total solid, and 4.79 ± 0.09 g/100 g for lactose; the total microbiological counts were 5.49 ± 2.119103 log cfu/mL, and the milk total somatic cell numbers were 85 ± 0.109103 cell/mL [10]. The pH of the milk was 6.60. From the obtained analysis, the raw goat milk fulfill the conditions according to the book of rules for hygienic criteria and milk quality [15, 17]. Given that the composition of milk is highly variable and depends on numerous genetic and paragenetic factors, its comparison shows great differences with the findings of other authors (**Table 1**).

Kashkaval, white-brined, and beaten cheese are the three main types of cheeses produced presently in Macedonia. The origin of beaten cheese is from the territory of Mariovo, produced in the past years on the pasture land only from ewe's milk. According to its salty taste and its hard consistency, it is an authentic product with characteristics that is preserved even in usual situations. The production of cheese

Characteristics	Mean \pm SD (n = 30)
Total solids	12.64 \pm 1.240
Fat	3.84 \pm 0.360
Protein	3.21 \pm 0.034
Casein	2.49 \pm 0.031
Lactose	4.49 \pm 0.077
Ash	0.75 \pm 0.027
pH	6.65 \pm 0.056

Adapted from [39]

Table 1.
Chemical composition of the goat milk.

has been carried out since the time of the Ottoman Empire. The “beaten” designation is originated from the one process step of the cheese production where the cheese curd is beaten to ensure proper draining (**Figure 4**) [18, 19].

Cilev et al. [5] investigated the chemical composition of goat milk on three farms during the month of April, and the highest percentage of milk fat is determined in milk from a farm in Kožle (3.85%), and the lowest percentage in milk is from a farm in Ajvatovci (3.50%). In terms of protein content, the highest percentage (3.70%) is determined to a farm in Taor, and the lowest is in the farm in Ajvatovci (3.05%). The content of lactose was highest in the farm in Ajvatovci (4.71%), while the lowest is from a farm in Taor (4.43%). The highest content of fat-free dry matter was found on the farm will be displayed (8.69%), while the lowest farm is Taor (8.26%). The total dry matter in milk was also highest in the farm will be displayed (12.42%) and the lowest farm is Taor (11.85%). In terms of the content of added water, the result charter in April in all three farms was zero, which indicated its full functionality in terms of physical water added.

Brined cheeses are with high salt content, which enables their preservation even in the warm periods of the year. They are produced from sheep, goat, and buffalo milk, as well as from their combinations. During the ripening, changes in the composition and properties of the cheeses are mutually dependent on changes in the brine [20–22].

In the last few years, the increased interest of the goat’s milk products on the marketplace and the scientific community is consistent with the general trend and efforts for the production of healthy food, since the goat’s milk has been well-known for its beneficial effects on human health [23]. According to statistics in 2011, white-brined cheeses are consumed in quantities of 7.4 kg per year, followed by 2.2 kg kashkaval cheese and urda (ricotta) with 2.1 kg by member of households [24].

Sulejmani [25] reported that white-brined cheeses have a high salt content that allows them to stay in the warm periods of the year. They are produced from sheep, goats, buffalo milk, and their combinations. In the ripening, changes in the composition and properties of the cheeses are mutually dependent on changes in the brine. Most varieties in this group are stored in closed containers, but some are stored in gas-permeable containers, which affect biochemical changes that occur in the process of ripening and storage.

The milk for beaten cheese manufacture is drained through cheesecloth (not obligatory) and poured into a curdling vessel. The curdling is most often done using enzymatic rennet with the strength of 1:5000 or the rennet chymosin CHY-MAX (2080 imcv/g) at the temperature of the milk of 25–35°C. In the past, for curdling homemade rennet was used obtained from the lamb’s stomach. The curdling process lasts 30–50 min. After that the curd is submitted to processing (churning or beating) using a wooden tool. The process of churning (beating) is done in 3 series of 50 strokes (150 strokes in total), and after each series, the curd is left to “rest” for 5–10 min. In this process it may come to separation of a part of the milk fat, in which case the fat is skimmed and removed from the vessel. When the beating process ends, the curdled mass is warmed up by adding warm water to the temperature of 53–90°C, depending on the particular manner of production [27] (**Figure 1**).

Recently consumers are more aware about the relationship between their eating habits and nutritional status. Consequently, they look for foods that are added with natural products rather than synthetic chemical compounds. Currently, they have interest in maintaining good health and an excellent body figure; therefore, they have become more careful in the food they choose to consume, looking for food with a high nutritional value, bioactive compounds, and antioxidant capacity, such as herbs, fruits, and vegetables. This is an opportunity for some local producers to manufacture cheese products with the partial or total replacement of

those chemical additives by natural herbal not only because of their antioxidant but also antimicrobial properties (**Figure 2**).

Antioxidant capacities of beaten goat cheeses, of 7 and 20 days ripened cheese (matured cheese), were higher than beaten cheese without plants (Sulejmani and Hayaloglu, unpublished data). Therefore, it could be hypothesized that consumption of matured white cow cheese could notably contribute to the body's antioxidant defense and prevention of diseases related to oxidative stress. However, further research is needed to elucidate the role of herbs in the antimicrobial and anticancer protective functions in human. *Origanum vulgare* is a perennial herbaceous plant, with wood stalk. The stub is usually gray-eyed. The roots are superficial, with a multitude of roots reaching at depths of 3–4 cm, and the plant is easily pulled. The flowers are short-tailed, gathered in a long spike in the midst of strong scent bows. It flourishes from the end of June and continues until the end of August.



Figure 1.
Typical beaten cheese production with a mixture of goat milk. After Sulejmani [26].



Figure 2.
Beaten goat milk cheese with *Origanum vulgare*.

Red oregano has reddish flowers and a pleasant smell. The flowers are full of nectar and are always frequented by bees. It is aromatic and spicy medicinal plants. The excellent ethereal oil is extracted from this. From 100 kg of dry matter, 2–2.25 kg of ethereal oil is extracted. Oregano on leaves and flowers contains etheric oils in various quantities consisting of a series of special value components. Essential oil (maximum 4%) may contain variable amounts of phenol, carvacrol, and timol. In addition, there are variants of monoterpenes, hydrocarbons (limonene, terpene, ocimene, caryophyllene, β -bisabolene, and p -cymene) as well as alcoholic monoterpene (linalool 4-terpineol). It has important properties, as antioxidants, antibacterial, antifungal, and anti-inflammatory and, recently, as anticancer. Oregano possesses powerful properties like antioxidants comparable to those of ascorbic acid and vitamin E. Carvacrols, thymol, and rosemary acids are the main components of essential oil. Known as a food supplements, carvacrol is a potent and bacteriostatic useful against mold and bacteria.

The influence of different heat treatments on goat milk was studied in detail [16]. Multiple analyses confirmed that the heat treatment of goat milk delays the initial coagulation and syneresis, and it improves the retention of dry matter, fat, and proteins. Therefore, on the basis of this finding, technological approaches of white-brined cheese were developed (**Figure 3**). The characteristic ability of goat milk proteins to retain water; the specific structure and the rheological properties of the cheese curd enable optimal regulation of the fermentation process of cheese and its salting. Traditionally, this type of cheese has been produced by local farmers on a small scale for decades using raw milk, and traditional techniques handed down from generation to generation using only elementary equipment. Instead of using a commercial starter culture, artisan cheese makers relies on the indigenous natural present microorganisms in the raw non-pasteurized milk and adventitious contaminants from the soil, equipment, surfaces, and the environment in general.

Sulejmani and Hayaloglu [18] investigated the use of raw and pasteurized goat milk in the production of Macedonian white cheese. Milk was collected from a certified organic farm from a Saanen goat's herd of a Novacani village (Veles, Macedonia). Two batches of cheeses from pasteurized (80°C for 2 min) (GP) and raw (GR) goat milk were produced traditionally using artisanal protocols. Goat milk coagulation was attained with commercial enzyme (1 g/100 per L milk) with a stated power of coagulating from 2235 IMCU/g (Chr. Hansen, Powder Extract CHY-MAX, Hørsholm, Denmark). The milk was coagulated at 32°C for 45 and 120 min for GR and GP cheeses, respectively. The coagulum was cut to medium-size (1–2 cm) grains. After whey removal by pressing, cheeses with block form weighing 0.5–1.0 kg were pressed for 4 and 8 h for GR or GP cheeses, respectively. At last, both cheeses were ripened in brine (15% w/v at 4°C) for 120 days.

The chemical composition of white-brined goat cheese made from pasteurized (GP) or raw (GR) milk at the first day was as follows: pH, 5.25 and 6.27; fat-in-dry matter, 37.86% (w/w) and 43.36% (w/w); dry matter, 32.60% (w/w) and 33.00% (w/w); fat, 12.38% (w/w) and 14.25% (w/w); and salt, 2.02% (w/w) and 2.73% (w/w), respectively. The use of pasteurization significantly affected the total solid, fat, moisture, and fat-in-dry matter contents of the cheeses ($P < 0.05$). The white cheese chemical composition was in compliance with the official bulletin [15]. Higher cheese pH levels were found in the cheeses made from raw milk (GR) compared with pasteurized milk (GP) ($P < 0.05$).

The values of WSN and 12% TCA-SN (expressed as percentage of TN) of both white goat cheeses are presented in **Tables 2** and **3**. The quantity of WSN and TCA-SN in the cheeses increased during ripening (until 60 days); however, after that, the increase was not intense during the end of ripening. After 60 days of ripening, GR cheeses had higher quantity of WSN than GP cheeses; also the highest

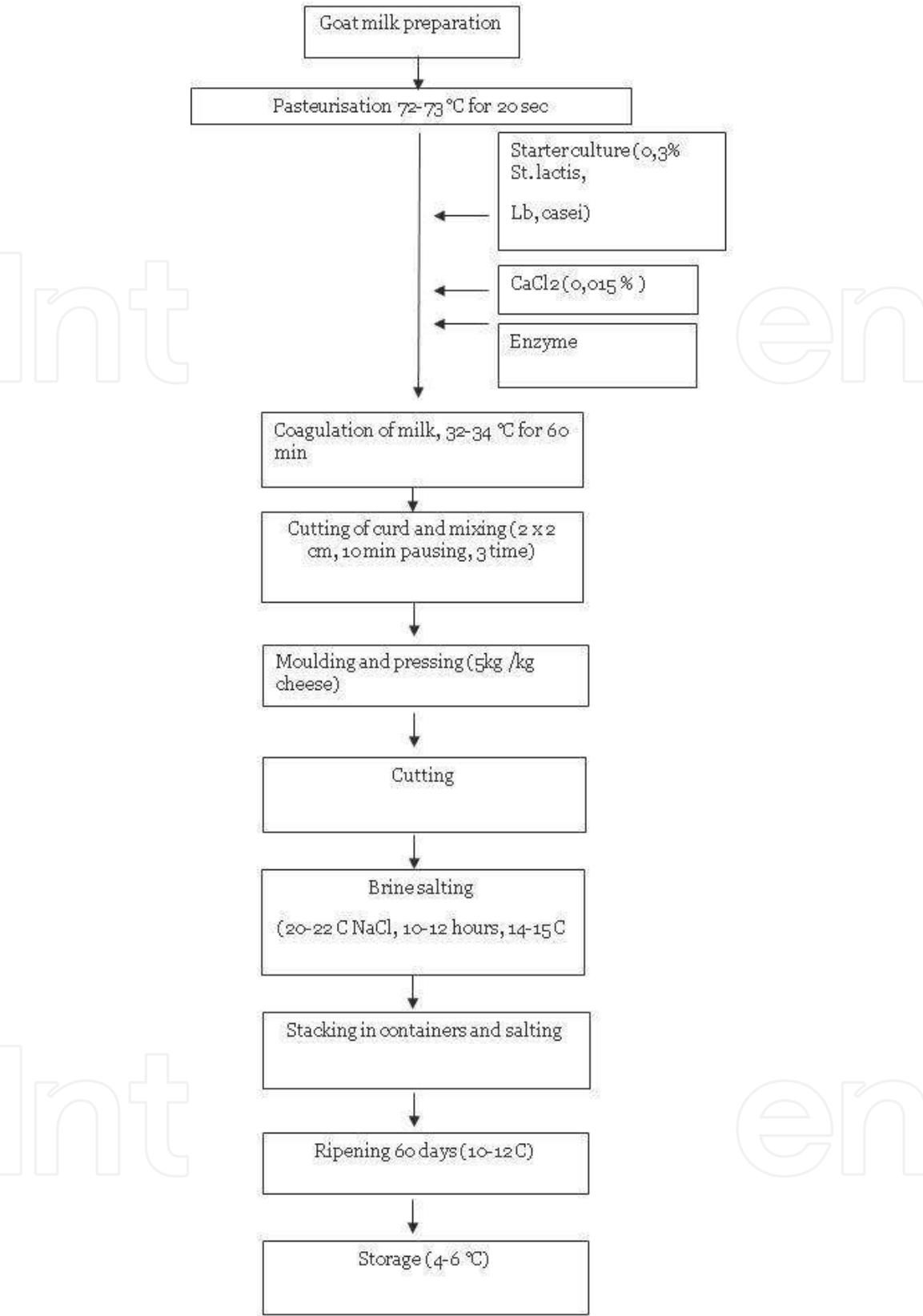


Figure 3.
Schematic illustration of white-brined cheese making [16].

TCA values were recorded at day 60 of ripening and then declined again. However, the quantities of WSN were higher in GR cheeses than in GP cheeses ($P < 0.05$). Higher and similar quantities of TCA-SN and WSN at 60 days of ripening were found in Teleme white-brined goat cheese, respectively [28].

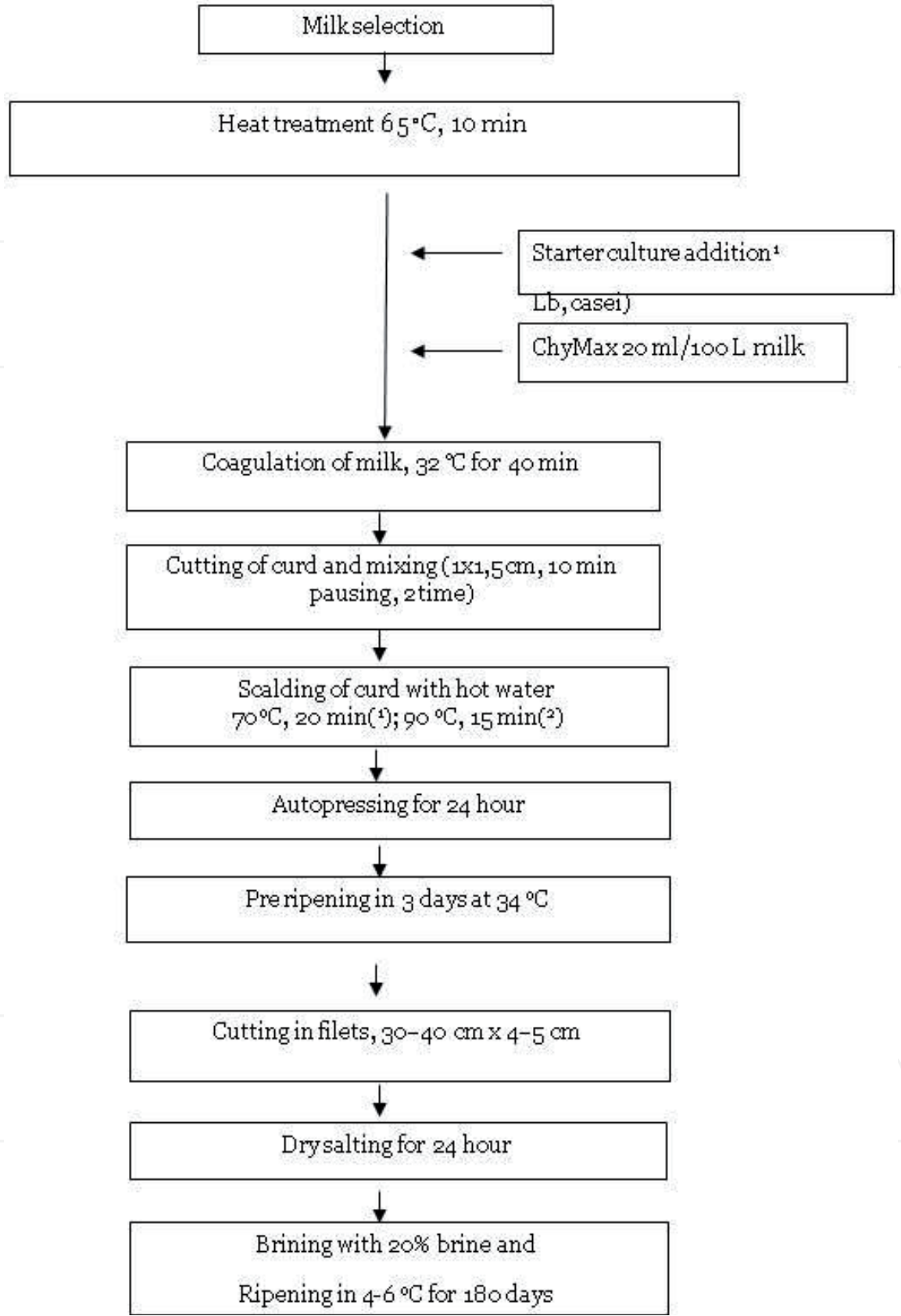


Figure 4.
Schematic illustration of industrial (1) and traditional (2) beaten cheese production using goat/ewes milk combination [26].

Most brine cheeses are dry-salted and are ripened and stored in brine, and the salting method is the basic difference in terms of varieties of cheeses. Traditionally, they are produced from sheep, cow, goat, or mixed raw milk [29, 30].

Parameters	Cheeses	Ripening time (days)		
		1	60	120
Total	GR	10.19 ± 0.95 ^{bA}	8.43 ± 0.04 ^{aA}	9.59 ± 0.79 ^{abA}
Protein	GP	10.13 ± 0.94 ^{aA}	9.90 ± 0.42 ^{aB}	10.88 ± 0.20 ^{aB}
WSN-SN	GR	7.74 ± 1.01 ^{aA}	8.64 ± 0.37 ^{aB}	7.31 ± 1.02 ^{aB}
(% of TN)	GP	5.82 ± 0.37 ^{bA}	6.22 ± 1.58 ^{bA}	2.93 ± 0.37 ^{aB}
TCA-SN	GR	2.44 ± 0.65 ^{aA}	3.05 ± 0.02 ^{aB}	2.92 ± 0.46 ^{aB}
(% of TN)	GP	1.71 ± 0.24 ^{abA}	2.39 ± 0.52 ^{bA}	1.44 ± 0.21 ^{aA}
TFAA	GR	0.41 ± 0.00 ^{eB}	0.30 ± 0.01 ^{aA}	0.44 ± 0.02 ^{dB}
mg Leu/g	GP	0.35 ± 0.00 ^{cA}	0.30 ± 0.00 ^{bA}	0.39 ± 0.01 ^{dA}

SD, standard deviation; TFAA, total free amino acid; DM, dry matter; WSN, water-soluble nitrogen. TN, total nitrogen; TCA, 12% trichloroacetic acid-soluble nitrogen. ^{a, d}Means ± SD within a row and ^{A-B}Means ± SD within a column with no common superscript capital letters differ (*P* < 0.05), respectively. Adapted from Sulejmani and Hayalogu [18]

Table 2.
Chemical parameters during ripening in raw (GR) and pasteurized (GP) white-brined goat cheeses.

Parameters	Kumanovo	Radovich
pH	5.01 ± 0.01	5.43 ± 0.05
% Lactic acid	1.73 ± 0.10	4.45 ± 0.13
Dry matter, %	68.43 ± 0.11	57.34 ± 0.21
Moisture, %	31.57 ± 0.11	42.67 ± 0.21
Fat, %	29.63 ± 0.25	26.00 ± 0.41
Fat(dm), %	43.29 ± 0.35	45.35 ± 0.84
Salt, %	4.11 ± 0.07	8.18 ± 0.38
Proteins, %	32.81 ± 1.09	21.32 ± 0.69
TN(g100 g ⁻¹ cheese)	5.15 ± 0.17	3.34 ± 0.11
WSN (% TN)	10.34 ± 1.06	32.76 ± 0.95
TCA-N (% TN)	6.37 ± 0.70	4.60 ± 0.04
TFAA(mgLeu/g)	3.18 ± 0.56	3.72 ± 0.13

Adapted from Sulejmani et al. [31]

Table 3.
Physical-chemical parameters of mixed goat/ewes milk cheese from different geographical locations.

At the beginning the ripening of white-brined goat cheese, as1-CN (f24–199) and c2-casein were produced, indicating high activity of chymosin and plasmin. However, it can be seen that b-casein reduction rate was smaller than as1-casein that of during ripening (**Figure 5**). After 60 days of ripening in the GR cheeses, the band corresponding to as1-I-casein (as1-CN f102–191) was present in all electrophoretograms of the samples, as a result of hydrolysis of as1- casein. A reduction of as1- and b-casein was obviously faster in the GR cheeses than in the GP cheeses, probably due to the native microorganisms and indigenous milk enzymes. Significantly inactivated indigenous and milk proteinases indicates on great impact that had pasteurization [30].

As it is obviously shown in **Figure 5**, the hydrolysis of as1-casein was faster in the GR cheeses during ripening obviously as a result of the higher activity of

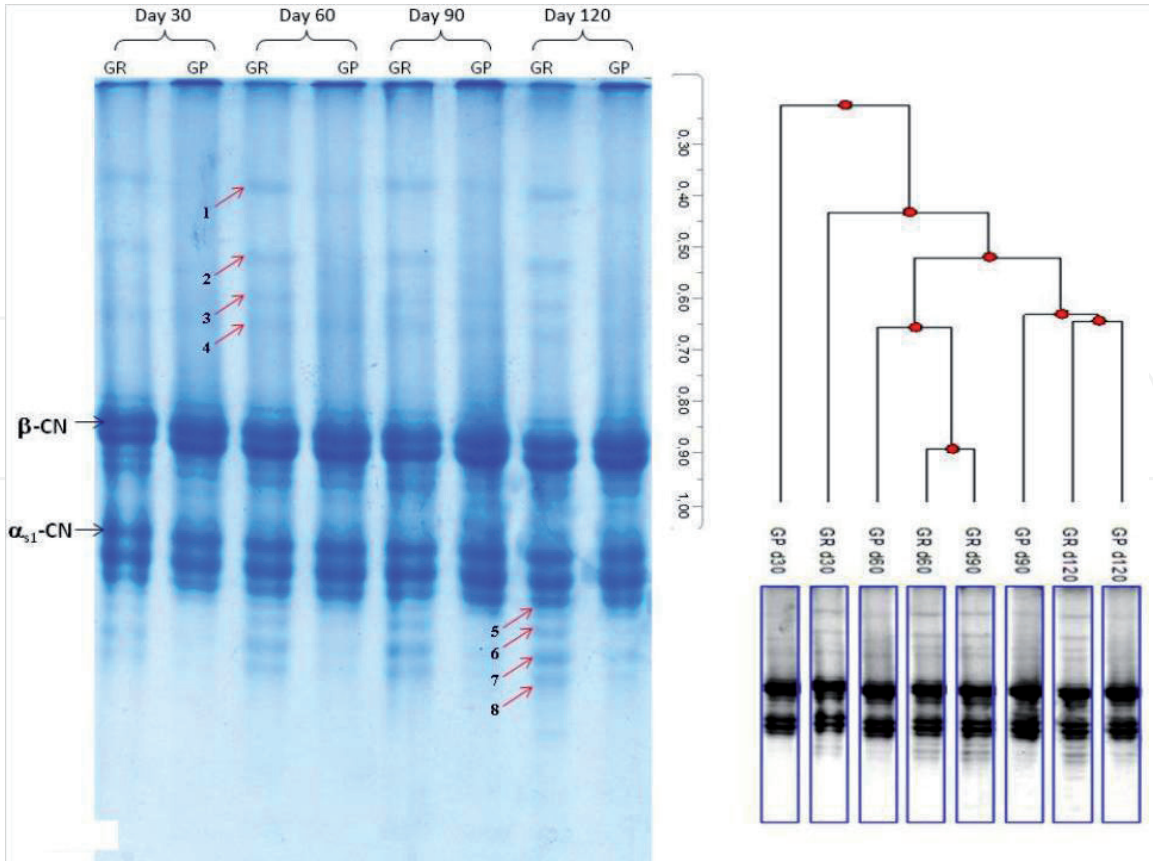


Figure 5. (Left) Urea-PAGE of the water-insoluble fractions of white goat milk cheeses made using raw (GR) or pasteurized (GP) method during 120 days of ripening (right) (with permission from John Wiley and Sons) [10].

indigenous proteinases in the curd, which is exactly associated with the heat degree of the milk heat.

Some differences were observed during ripening for the fractions of peptides, which were eluted in the GR cheeses at higher quantity at the end of ripening than the beginning of ripening. Common peaks were evident in the 30 and 60 days of ripening in all of the chromatograms, with an increase in concentration of peptides during ripening, which were mainly eluted between the 56th and 76th min. In the chromatogram, between 64 and 74 min, the peak heights in the cheeses were generally much higher than in other cheese samples until the 120th day of ripening (Figure 6).

The analysis of free amino acids in white-brined goat cheese confirmed the presence of all amino acids except tyrosine (Table 4). The quantity of free amino acids is low because of particular process of fermentation. Due to the high concentration of salt and low ripening temperature of white brine, the participation of thermophilic lactic acid bacteria in ripening is minimal, and this cheese is defined by a weaker breakdown of paracasein.

The volatile components of white-brined goat cheeses have not previously been studied. They consisted of 12 acids, 14 esters, 6 ketones, 3 alcohols, 4 terpenes, and 6 miscellaneous compounds (Table 2). Acids, alcohols, and ketones constituted the principal chemical groups during ripening (mean volatile concentration of 51, 16, and 12% w/w of total compounds, respectively). The raw goat milk (GR) cheeses were by a higher quantity (78%) of total volatile compounds than the pasteurized goat milk (GP) cheeses, during ripening. Compared with day 1, a significant decrease in the total quantity of volatile compounds (except ketones and alcohols) was found after 120 days of ripening. Carboxylic acids are the principal volatile

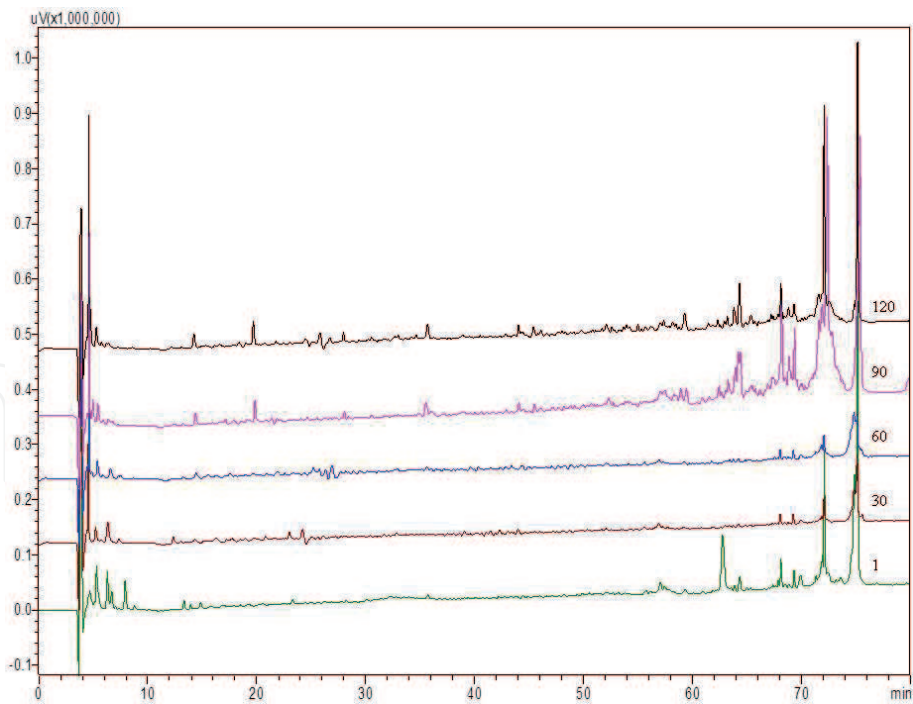


Figure 6. Reverse-phase HPLC profiles of the water-soluble fraction of white goat milk cheeses made using raw milk during 120 days of ripening [10].

Free amino acids mg %	Ripening	
	Day 15	Day 60
Lysine	16.2 ± 0.31	33.11 ± 0.41
Histidine	2.2 ± 0.13	16.12 ± 0.71
Arginin	2.7 ± 0.71	4.85 ± 0.27
Threonine	2.60 ± 0.78	3.71 ± 0.62
Valin	11.78 ± 0.61	14.80 ± 0.16
Metionin	6.11 ± 0.43	8.71 ± 0.62
Isoleucin	3.21 ± 0.62	4.52 ± 0.27
Leucine	11.72 ± 0.31	21.57 ± 0.36
Phenylalanine	4.11 ± 0.62	15.61 ± 0.31
Total essential amino acids	60.63 ± 0.64	123.01 ± 0.74
Asparagin acid	3.8 ± 0.11	9.11 ± 0.37
Serin	6.10 ± 0.18	12.11 ± 0.38
Glutamic acid	6.70 ± 0.79	9.28 ± 0.65
Proline	1.50 ± 0.28	3.61 ± 0.33
Glycine	—	6.63 ± 0.58
Alanin	3.31 ± 0.41	4.11 ± 0.43
Cistin	4.81 ± 0.11	7.51 ± 0.38
Tirozin	—	—
Total nonessential amino acid	26.22 ± 0.53	52.36 ± 0.59
Total quantity	89.18 ± 0.58	176.32 ± 0.71

Adapted from Srbinovska [16]

Table 4. Free amino acid concentration in white-brined goat cheese.

class in Macedonian white goat cheese (with 51% of total volatile compounds). The raw goat milk (GR) cheeses were characterized by higher quantity (86%) of total acids than the pasteurized goat milk (GP) cheeses during ripening. Milk heat treatment significantly ($P < 0.05$) influenced the concentrations of two volatile fatty acids (hexanoic acid and octanoic acid) (**Table 2**). Similarly, these compounds have been shown to be the principal volatile class in other goat milk cheeses [32]. The main acid was hexanoic acid (40% of total acids), and this was identified at significantly higher quantity in GR cheeses at 60 days of ripening. 3-Methylbutanoic acid was the most abundant branched chain fatty acid found in Macedonian goat cheese. This is in agreement with the findings of Beuvier et al. [33]. During ripening, total acids were at a higher concentration in the GR cheeses (86%) in comparison with GP cheeses (14%).

Caproic acid is a product of lipolysis, which significantly contributes to the smell of goat cheese [33]. Karagul et al. [34] explored the level of proteolysis in “Ezine” cheese, produced from a mixture of goat milk (40%), sheep’s milk (45–55%), and cow’s milk (up to 15%) without starter culture, during 8 months ripening. Urea-PAGE assay confirmed that α -casein decomposes very quickly, while the β -casein degradations are almost constant. Differences in the rate of degradation are associated with pH and salt content [35].

Flavor is the main properties that influence the selection and consumption of cheeses. The effect of fatty acids on the sensory properties of different types of goat milk cheese is essential. The concentration of butyric acid is increased during the ripening of cheeses mainly higher of 50% from the total concentration in the beginning of its production (mozzarella 66.35%, white-brined 74.58%, and pecorino 51.28%) [9]. The reason for the lower degree of formation of butyric acid during ripening and especially at the end of ripening of the cheeses is assumed to be the lack of a free substrate for conversion into fatty acids by way of lipolysis or reduction of enzyme activity due to the change in the microstructure of the cheeses.

At the first day of ripening in the raw goat milk cheeses (GR), acetic acid was identified at a higher concentration. Alcohols are the second most significant volatiles (16%) isolated in Macedonian goat cheese. At the end of ripening, the concentration of alcohols decreased to 40%, while after 60 days of ripening their quantity was 50%. The total esters were at higher quantity (98%) in raw goat milk (GR) cheeses than pasteurized goat milk (GP) cheeses during ripening. At the 60th day of ripening, a very high quantity of 3-methyl-1-butanol was found in the GR cheeses (**Table 5**). Heat treatment of the curd did not affect branched alcohols (except 2-ethyl-1-hexanol). 2-Propanone and 2-heptanone were the most abundant ketones among total of six ketones representing 54% and 13% of the total quantity of ketones, respectively. Higher quantity (77%) of total esters was characterized in the raw goat milk (GR) cheeses rather than the pasteurized goat milk (GP) cheeses during ripening. Because of particular odors and low perception thresholds, ester is very significant compounds in dairy products [36]. 2-Propanone and 2-heptanone were predominant ketones among six ketones that were identified in the Macedonian white goat cheeses.

Five different acids that were identified in the Goat beaten cheese from Kumanovo region with concentration of $13347.2 \mu\text{g } 100 \text{ g}^{-1}$ were reported. Six different acids were identified in the goat beaten cheese from the Radoviš region, and their concentration were $13773.8 \mu\text{g } 100 \text{ g}^{-1}$, respectively [31]. Hexanoic, octanoic, and decanoic acids were responsible for the characteristic aroma of goat cheeses, and their contribution to the volatile profile of beaten cheeses has been shown in this study as well, giving rise to the trivial terms caproic, caprylic, and capric acids, respectively. In addition 2-heptanone was identified at highest concentration in

Compounds	RI	Day 1		Day 60		<i>P (type)</i>
		GP	GR	GP	GR	
<i>Acids</i>						
2-Hydroxypropanoic acid	8186	0.28 ± 0.40	101.04 ± 12.89	ND	ND	NS
2-Ethylbutanoic acid	20,383	59.36 ± 8.95	ND	ND	ND	NS
Isobutyric acid	26,446	ND	13.75 ± 9.44	ND	ND	NS
Butanoic acid	28,317	ND	79.65 ± 12.64	47.89 ± 6.72	18.27 ± 9.73	NS
Pentanoic acid	28,405	ND	8.18 ± 1.57	ND	ND	NS
3-Methyl, butanoic acid	29,400	ND	1.35 ± 1.1	32.01 ± 3.64	16.19 ± 9.84	NS
Hexanoic acid	33,722	ND	182.58 ± 19.81	46.86 ± 6.91	260.64 ± 127.86	*
Acetic acid	37,692	ND	5.28 ± 7.47	ND	ND	NS
Octanoic acid	38,524	ND	112.40 ± 18.96	ND	180.47 ± 174.55	*
Isobutyric acid	41,235	ND	11.13 ± 1.74	ND	ND	NS
Decanoic acid	42,882	ND	45.36 ± 6.14	ND	ND	NS
2-Ethyl, caproic acid	45,717	ND	17.62 ± 13.39	ND	10.68 ± 5.10	NS
<i>Total</i>		59.6 ± 9.3	578.3 ± 47.9	126.7 ± 16.2	486.2 ± 324.1	
<i>Ketones</i>						
2-Propanone	6352	18.19 ± 3.11	64.82 ± 37.66	12.82 ± 5.71	51.55 ± 33.87	*
2-Butanone	7706	1.68 ± 0.49	4.23 ± 1.21	3.89 ± 0.26	3.76 ± 1.24	NS
2-Pentanone	9446	3.40 ± 2.46	7.22 ± 4.97	6.65 ± 1.36	8.65 ± 3.60	*
2-Heptanone	15,472	1.93 ± 2.16	3.48 ± 3.12	ND	19.87 ± 7.07	NS
2-Octanone	15,501	ND	ND	0.98 ± 0.39	ND	NS
2-Nonanone	21,938	ND	ND	ND	8.38 ± 7.24	NS

Compounds	RI	Day 1		Day 60		<i>P (type)</i>
		GP	GR	GP	GR	
<i>Total</i>		25.12 ± 12.3	79.15 ± 55.8	24.3 ± 13.3	92.5 ± 55.9	
<i>Esters</i>						
Methyl acetate	6521	3.35 ± 1.90	9.12 ± 1.90	3.17 ± 1.58	6.51 ± 1.12	*
Ethyl acetate	7447	19.43 ± 14.40	2.14 ± 3.03	2.24 ± 1.88	6.18 ± 6.79	NS
Methyl propanoate	7823	1.86 ± 0.86	4.56 ± 0.58	2.30 ± 1.69	3.71 ± 0.21	NS
Methyl butyrate	9645	2.28 ± 0.69	12.98 ± 5.42	3.69 ± 4.12	14.19 ± 6.39	*
Methyl carbonate	9785	0.15 ± 0.21	2.70 ± 0.18	ND	ND	NS
Ethyl butyrate	11,035	1.65 ± 2.34	ND	ND	ND	NS
n-Butyl acetate	12,024	1.04 ± 1.47	ND	ND	ND	NS
Isoamyl acetate	13,535	1.59 ± 2.24	ND	ND	ND	NS
Methyl caproate	15,544	0.34 ± 0.49	2.56 ± 3.63	ND	ND	NS
Ethyl heptanoate	15,973	ND	23.29 ± 32.93	ND	ND	NS
Isoamyl acetoacetate	16,141	0.72 ± 1.02	ND	ND	ND	NS
Ethyl n-caproate	17,021	0.17 ± 0.25	ND	ND	ND	NS
Dimethyl phthalate	24,779	1.74 ± 2.46	3.16 ± 4.47	ND	ND	NS
Diethyl phthalate	45,468	1.77 ± 1.18	25.06 ± 26.41	1.25 ± 1.77	1.11 ± 1.56	NS
<i>Total</i>		36.10 ± 29.51	85.58 ± 78.56	12.65 ± 11.04	31.70 ± 16.07	
<i>Terpenes</i>						
dl-Limonene	15,942	54.96 ± 7.07	ND	109.79 ± 31.99	ND	*
Cymene <para->	18,287	1.80 ± 2.54	ND	ND	ND	NS
Alph.-thujene	14,771	0.10 ± 0.14	ND	ND	ND	NS

Compounds	RI	Day 1		Day 60		P (type)
		GP	GR	GP	GR	
Alpha-pinene	10,644	15.61 ± 10.93	14.80 ± 6.62	49.14 ± 30.44	6.66 ± 0.37	NS
<i>Total</i>		72.47 ± 20.67	14.80 ± 6.62	158.92 ± 62.44	6.66 ± 0.37	
<i>Alcohols</i>						
Ethanol	8302	1.79 ± 0.05	3.85 ± 5.44	ND	1.70 ± 1.10	NS
3-methyl, 1-butanol	16,117	1.06 ± 1.50	49.01 ± 5.25	ND	233.12 ± 155.11	*
1-Pentanol	17,429	ND	2.66 ± 0.24	ND	ND	NS
<i>Total</i>		2.84 ± 1.54	55.52 ± 11.93	ND	234.81 ± 156.22	
<i>Miscellaneous</i>						
Pentane	4767	0.24 ± 0.34	6.08 ± 8.60	5.49 ± 4.21	ND	NS
Hexane	4905	7.67 ± 3.73	2.33 ± 0.31	4.56 ± 1.43	3.34 ± 2.89	NS
Dimethyl sulfide	5742	ND	6.56 ± 9.28	3.44 ± 3.20	ND	NS
Methylamine-D2	7583	1.22 ± 1.72	6.76 ± 0.88	9.96 ± 4.63	8.05 ± 4.23	NS
2-Methylbutanal	7976	0.48 ± 0.43	4.90 ± 4.14	ND	2.96 ± 3.21	*
3-Methylbutanal	8064	4.10 ± 3.57	35.28 ± 12.13	3.94 ± 1.56	29.09 ± 30.27	**
<i>Total</i>		13.7 ± 5.7	61.5 ± 26.4	27.3 ± 9.3	45.0 ± 37.7	NS

Mean data for three batches of pasteurized (GP) and raw (GR) goat cheese analyzed in triplicate. RI, retention index; ND, not identified; NS, not significant; P, probability. P age is probability for ripening period (i.e., 1, 60, or 120 days), P type is probability for cheese type (i.e., GP or GR) [10].

*P < 0.05.

**P < 0.01.

Adapted from Sulejmani and Hayaloglu, 2017

Table 5.

Mean values ± SD of volatile compounds identified in pasteurized (GP) and raw (GR) white goat's milk cheeses after 1 and 60 days of ripening (µg/100 g).

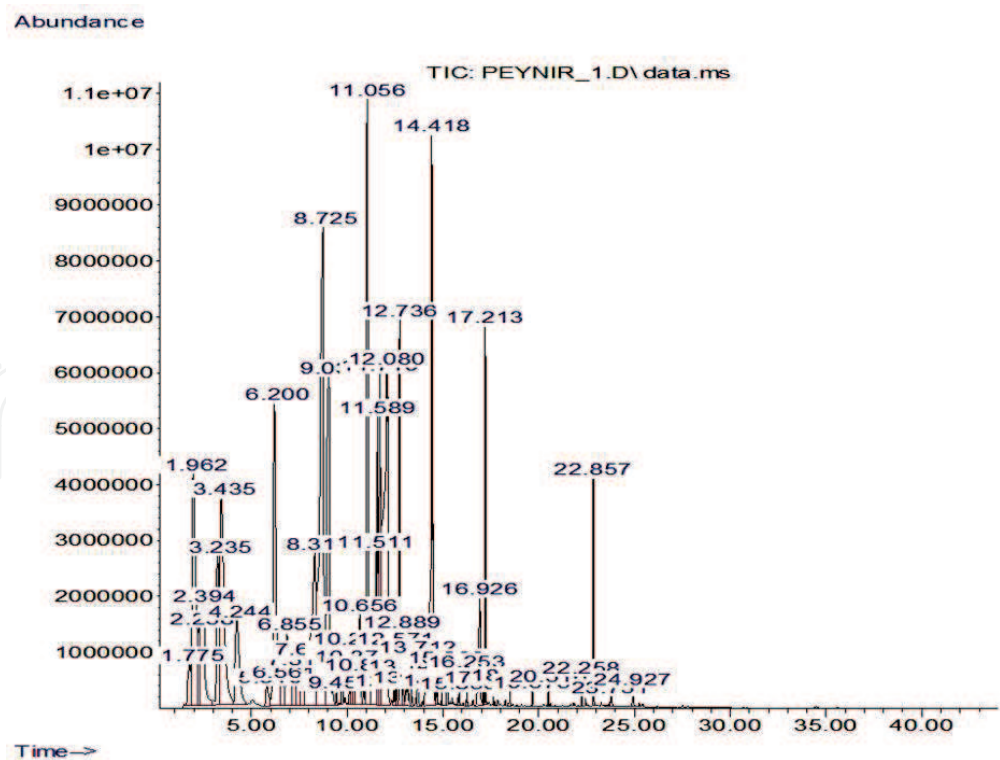


Figure 7.
GC-MS chromatogram of volatiles compounds identified from goat beaten cheese [21].

Kumanovo beaten cheese than other regions (**Figure 7**). Also 2-octanone, 8-nonen-2-one, and 2-nonanone were rarely found in cheeses from other regions.

Heptanol is determined in highest amount in the beaten cheese with goat milk from the northeast region and has been identified as a key aromatic flavor- component in gorgonzola and grana padano cheese [37]. Curioni and Bosset [38] reported a high concentration of heptanols as well as in semihard varieties of Spanish cheese from goat's milk.

4. Conclusions

The breeding of the goats in the Republic of Macedonia has a mark of tradition, namely, because of appropriate grazing conditions. This is very economical, because the entire diet is reduced to a grazing with less extra feed in the form of concentrate and minerals. Also Macedonia has real possibilities for transformation of many extensive goat farms into an organic farm. In addition, it creates additional opportunities for the outlay on the markets in the EU, for which the organic production year-by-year increases. Macedonian goat cheeses are being differentiated by their strong bounds with the territory of their origin, and so they represent a historical and cultural designation of the community which they are produced by. Production of these cheeses is in limited geographical areas with use of know-how techniques transferred from generation to generation and use of milk that has undergone no treatment after milking. Goat milk can be successfully used to produce various cheeses because cheese is characterized by a specific lactic acidic taste and aroma, a good degree of protein breakdown. Lactic acid processes and changes in moisture content take place more evenly during ripening than cow cheeses. From milking to the end of ripening process, this type of cheeses is passing through different surroundings where a variety of microorganisms have an opportunity to grow and develop. The research that has been conducted has shown that traditional

made cheeses have unique benefits in terms of palatable pleasure, richness, and diversity as well as protection against pathogens. Undoubtedly their properties have been achieved due to the presence of unique indigenous microbiota especially because of the use of raw milk, combined with specific skills that give their general characteristic properties and quality. In order to understand the situation of traditional milk processing and utilization in this part of the state, one should recall that milk production has an obvious seasonality related to climatic conditions and most of these products are homemade following neither standardized conditions nor proper hygiene standards. Careful attention must be paid to hygiene in order to produce milk of high bacteriological quality. However, despite all precautions, it is impossible to completely exclude bacteria from milk. Therefore, good hygiene is particularly important in producing especially fresh ripened cheeses. So prevention of contamination of the milk and meticulous attention to good hygiene during cheese production and ripening will reduce the incidence of pathogens; therefore, good acid-produced cheese during proper ripening is also helpful.

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